

APPLICATIONS OF TOROIDS IN HIGH-PRESSURE NMR SPECTROSCOPY

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Abstract

Toroid detectors have distinct NMR sensitivity and imaging advantages. The magnetic field lines are nearly completely contained within the active volume element of a toroid. This results in high NMR signal sensitivity. In addition, the toroid detector may be placed next to the metallic walls of a containment vessel with minimal signal loss due to magnetic coupling with the metal container. Thus, the toroid detector is ideal for static high pressure or continuous flow monitoring systems. Toroid NMR detectors have been used to follow the hydroformylation of olefins in supercritical fluids under industrial process conditions. Supercritical fluids are potentially ideal media for conducting catalytic reactions that involve gaseous reactants, including H_2 , CO, and CO_2 . The presence of a single homogeneous reaction phase eliminates the gas-liquid mixing problem of alternative two-phase systems, which can limit process rates and adversely affect hydroformylation product selectivities. A second advantage of toroid NMR detectors is that they exhibit a well-defined gradient in the rf field. This magnetic field gradient can be used for NMR imaging applications. Distance resolutions of $20\ \mu$ have been obtained.

Introduction

The vitality of the industrial process arena is strongly influenced by the development of new instrumental techniques. This work focuses on a special type of NMR detector whose unique properties make it an ideal choice for *in situ* NMR spectroscopic analysis of synthesis gas reactions. In addition, the same toroid NMR detectors are useful for imaging applications. In contrast to conventional NMR imaging techniques, the new toroid cavity NMR-imaging method retains all chemical shift and coupling constant information.

High-pressure NMR spectroscopy

One of the key properties of toroids for NMR applications is that the magnetic field lines are nearly completely contained within the windings of the coil. This contrast with the Helmholtz and solenoid coils that are typically used in commercial NMR spectrometers. In the latter type of coils, the magnetic field lines are more diffuse and extend well outside the coil windings, see Figure 1. The result is a signal-to-noise advantage of 3-5 for toroids compared with Helmholtz detectors [1-3]. More significantly for high pressure work, a toroid detector may be operated near the walls of a metallic containment vessel. Thus, in the cell design [4] of Figure 2, there is minimal dead volume. Furthermore, the small internal reactor volume of only 8 ml minimizes the amount of hazardous materials required for the experiments. The reactor in Figure 2 is routinely operated at 250 °C and 300 atm pressure. Typical *in situ* spectroscopic results obtained during the hydroformylation of propylene [5,6] are presented in Figures 3 and 4.

Special emphasis has been placed on exploring the use of supercritical fluids as homogeneous reaction media for catalytic synthesis gas transformations. Supercritical fluids consisting of carbon dioxide or water are environmentally benign solvents. Furthermore, separations of products may be accomplished by facile pressure alterations [7] instead of energy intensive distillations. In addition, mixing is not required for supercritical fluids. The oxo process is an important industrial reaction that is sensitive to gas-liquid mixing conditions [8]. Interestingly, we have found that the reaction exhibits improved straight chain aldehyde product selectivity [5,6] when the reaction is conducted in supercritical carbon dioxide as indicated in the last row of Table 1.

Supercritical fluids also have advantages for fundamental mechanistic analyses. Thus, the low viscosity of supercritical fluids results in NMR linewidths that are up to an order of magnitude sharper than those found in conventional organic solvents [5,9]. Thus, in benzene solvent where the ^{59}Co NMR linewidths are broader than those in Figure 4 by a factor of six, it would be difficult to resolve $HCo(CO)_4$ and $Co_2(CO)_8$. Furthermore, the acyl intermediate would not be detectable. The oxo process was investigated by a combination of

^1H , ^{13}C , and ^{59}Co spectroscopy under industrial process conditions. It was found that the high temperature reaction chemistry is dominated by mechanistically significant $\cdot\text{Co}(\text{CO})_4$ radical concentrations which are formed by homolysis of the Co-Co bond in $\text{Co}_2(\text{CO})_8$. The Co-Co bond dissociation enthalpy in $\text{Co}_2(\text{CO})_8$ has been measured, $\Delta H^\circ = 19 \pm 2$ kcal/mole and $\Delta S^\circ = 29 \pm 4$ cal/(K·mol), by NMR magnetic susceptibility measurements over the temperature range of 120 to 225°C and from the contact chemical shift of the carbon monoxide ligand in the ^{13}C NMR spectra, $\Delta H^\circ = 19 \pm 2$ kcal/mole. The $\cdot\text{Co}(\text{CO})_4$ radical induces a complex manifold of facile hydrogen atom transfer reactions that may be quantitated by ^1H and ^{59}Co NMR line shape analysis [10].

NMR-Imaging

Toroid cavity detectors may be used for rotating frame spectroscopic imaging [11]. The well-defined rf field gradient that is produced within a toroid cavity [12] minimizes the problems that were encountered in early applications of the rotating frame imaging technique using surface coils [13]. The salient feature of the rotating frame imaging technique is that the high-resolution NMR spectral information is not lost as is the case in conventional magnetic resonance imaging (MRI). As an example, five capillaries containing different solvents were placed at a spacing of 0.8 mm outward from the center of the cavity. The result in Figure 5 demonstrates that in a single experiment, the toroid cavity imaging technique can chemically distinguish between water and acetone, in addition to identifying the location of these samples along the distance axis. The chemical shift resolution of this technique is equivalent to that of a normal NMR spectrum. Alternatively, the ultimate resolution with respect to distance for the toroid cavity detector is under study. The data in Figure 6 demonstrates the distance resolution by ^{19}F NMR spectroscopy of two Teflon layers that were placed around the central conductor of the toroid cavity resonator. The measured thickness of the Teflon layers, as well as their 20 μm separation, is accurately reproduced by the imaging data. This distance resolution is already better than that which can be attained for solid samples using conventional MRI techniques. This toroid cavity imaging technique could find a wide range of applications in the characterization of surface layers and in the production of advanced materials. Potential areas of application include *in situ* NMR monitoring of growth sites during ceramic formation processes, analysis of the oxygen annealing step for wires coated with high-temperature superconductors, investigation of the reaction chemistry as a function of distance within the diffusion layer for electrochemical processes.

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Table 1. Selectivity in the Hydroformylation of Propylene

Solvent	n/i-Butyraldehydes
2,2,4 - Trimethylpentane ^a	4.6
Benzene ^a	4.5
Toluene ^a	4.4
Diethyl ether ^a	4.4
Ethyl alcohol, 95% ^a	3.8
Acetone ^a	3.6
Commercial plants ^b	3.0 - 4.1
CO ₂ (0.5 g/ml) ^c	7.2

^a T = 108 °C, P(CO) = 140 atm, P(H₂) = 100 atm, ref 14.

^b T = 140-180 °C, P(CO) = 100-150 atm, P(H₂) = 100-150 atm, ref 15.

^c T = 80 °C, P(CO) = 56.1 atm, P(H₂) = 56.1 atm, ref 5,6.

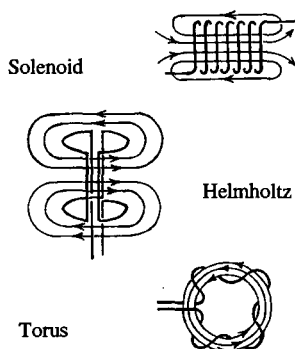


Figure 1. NMR detector coils.

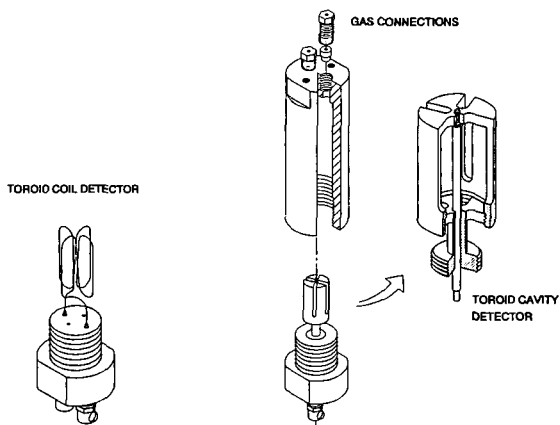


Figure 2. High-pressure NMR cell with toroid coil or cavity detector.

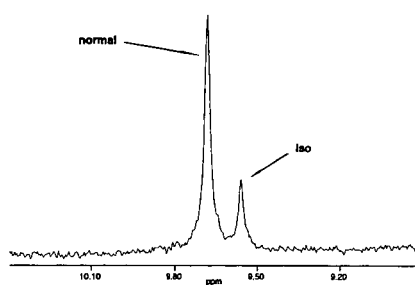
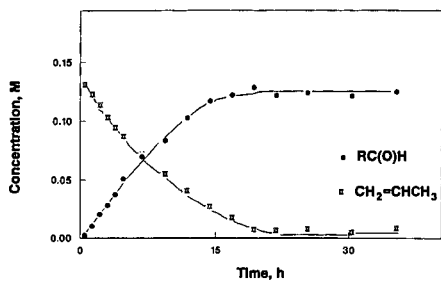


Figure 3. Butyraldehyde product mixture based on *in situ* ^1H NMR spectra during the hydroformylation of propylene in supercritical carbon dioxide at 80 $^\circ\text{C}$.

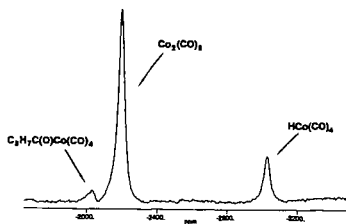
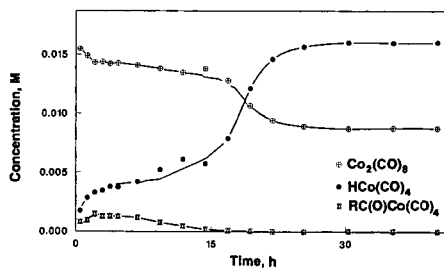


Figure 4. Organocobalt intermediates based on ^{59}Co NMR spectra during the hydroformylation of propylene in supercritical carbon dioxide at 80 $^\circ\text{C}$.

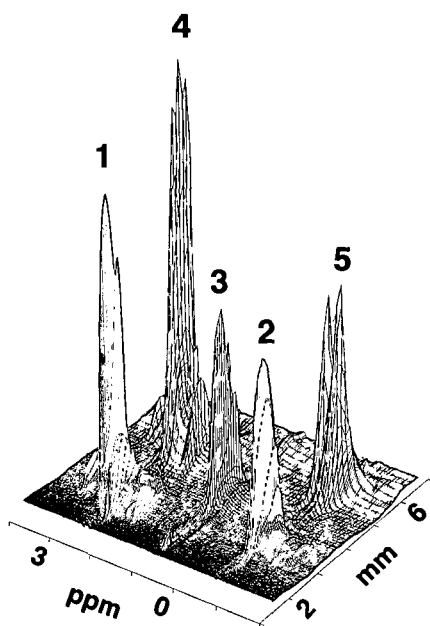


Figure 5. Simultaneous resolution of NMR chemical shift and radial displacement for five capillary tubes containing: 1, water; 2, isopropanol; 3, acetone; 4, water; and 5, isopropanol.

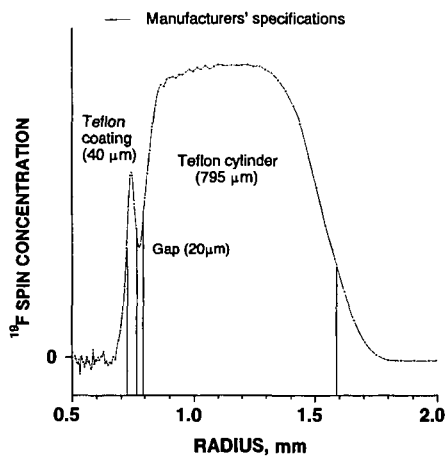


Figure 6. Plot of teflon concentration versus radial displacement based on ^{19}F NMR imaging.